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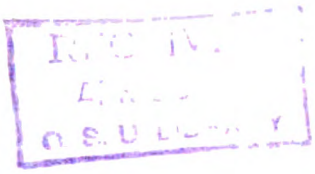
MINOR MINERAL FERTILIZER MATERIALS



BY

BERTRAND L. JOHNSON

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DEPARTMENT OF THE INTERIOR - BUREAU OF MINES

MINOR MINERAL FERTILIZER MATERIALS[1]

By Bertrand L. Johnson[2]

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FOREWORD

The major elements essential to plant growth are nitrogen, potassium, and phosphorus. These three constituents of the soil are removed relatively rapidly by growing crops and consequently are the main constituents of commercial fertilizers. Scientific studies, however, have progressively revealed the fact that a number of other plant foods, many of which are not necessarily supplied in commercial fertilizers, are necessary to assist plant growth and fruit production and that soils deficient in certain of these minor elements may be made much more productive by adding them.

The farmer looks to the miner to furnish most of the elements requisite to plant growth, which have to be supplied through the medium of fertilizer additions. It follows that the mining industry should keep an eye upon developments in the fertilizer industry and in the results of soil studies as a possible outlet for mineral products. The important industries engaged in the production and marketing of the three principal plant nutrients have already been described in Bureau of Mines publications.3/ The present paper discusses the commercial implications with respect to other elements that are now employed as soil additions.

GENERAL DISCUSSION

Fertilizing materials are those substances which, under favorable conditions, will when added to the soil produce a better growth of crops through direct or indirect action (1) either on the crop or (2) on the properties of the soil.4/ Direct fertilizers contain essential plant-food or nutrient elements available at once or made so under favorable soil conditions.5/ Indirect fertilizers (known also as soil amendments) are added to soils to modify the physical or chemical conditions of the soil to produce some effect beneficial to plant growth.

Many elements have been found in plants growing naturally on the soil. These include aluminum, arsenic, barium, boron, bromine, calcium, carbon, chlorine, cobalt, copper, fluorine, hydrogen, iodine, iron, lead, lithium, magnesium, manganese, nickel, nitrogen, oxygen, phosphorus, potassium, rubidium, silicon, sodium, strontium, sulphur, titanium, and zinc.

Of these various elements it is at present believed that not over 14 - carbon, hydrogen, oxygen, nitrogen, phosphorus, potassium, calcium, magnesium, iron, sulphur, manganese, boron, copper, and zinc - are necessary to normal

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3/ Johnson, Bertrand L. Nitrogen and Its Compounds: Inf. Circ. 6385, Bureau of Mines, 1931, 33 pp.
_____ Phosphate Rock. Part I, General Information: Inf. Circ. 6255, Bureau of Mines, March 1930, 64 pp.
_____ Potash: Econ. Paper 16, Bureau of Mines, 1933, 78 pp.

4/ Van Slyke, L. L., Fertilizers and Crop Production: Orange Judd Pub. Co., New York, 1932, p. 157.

5/ Van Slyke, L. L., work cited, p. 159.

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plant growth. The other elements listed as present in plants are not intentionally utilized as plant foods in agricultural practice, their application at present not being regarded as of economic importance. In many instances, however, some of them have been added to the soil involuntarily, either as impurities in various fertilizers or as constituents of compounds containing other desired elements. Compounds of many of these so-called unessential elements have, however, been tested as to their effect on plant growth at various agricultural experiment stations.

Carbon, hydrogen, and oxygen are obtained from the air. Nitrogen is obtained by the plants both directly and indirectly from the air and also from organic and inorganic compounds in the soil. The other elements may be furnished by the soil or may be supplied entirely by addition of minerals. Such large amounts of nitrogen, phosphorus, and potassium are required by plants that they usually have to be added to soils as artificial fertilizers to obtain maximum crop yields. Formerly these major nutrients were considered the only essential elements needed.

A limited number of elements (calcium, magnesium, and sulphur) function as indirect fertilizers (soil amendments). Calcium and sulphur are contained in practically all mixed fertilizers, although often they are not mentioned. Magnesium is needed as a plant food in many soils and is used increasingly in fertilizers; it has been described as the fourth major plant food.

The individual roles of specified elements are discussed on subsequent pages of the present paper, but for further study of the general subject of minor elements in plant nutrition the reader may consult the following list of references:

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CALCIUM

Calcium is applied to the soil in such diverse compounds as limestone, dolomite, oyster and clam shells, calcareous marl, air-slaked lime, gypsum and anhydrite, superphosphate, phosphate rock, dicalcium phosphate, quicklime, and water-slaked lime. Quicklime, air-slaked lime, and water-slaked lime are, of course, prepared from various calcium carbonate materials. Superphosphate and dicalcium phosphate result from chemical treatment of phosphate rock. Ground phosphate rock, which contains the calcium as calcium phosphate, and its derived product, superphosphate, which contains the calcium both as phosphate and as sulphate, are generally used only to supply phosphorus as a plant food and not for their calcium content. The amount of gypsum applied to the soil in superphosphate is said to be insufficient to have a marked effect, as an indirect fertilizer, on soil acidity.

Calcium compounds are the principal and most widely used soil amendments but are used much less frequently solely to supply calcium directly as plant food to crops, as that element is generally present in arable soils in sufficient quantities to supply plant growth fully.

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As indirect fertilizers calcium compounds are said to have several functions, as follows:

1. Correction of soil acidity, by furnishing a base to combine with soil acids. This is the principal use. Calcium, being the cheapest of the available bases (calcium, magnesium, sodium, and potassium) for the correction of soil acidity, is the usual corrective applied. Only the calcium carbonate materials and their derived products, quicklime and slaked lime, are used for this purpose.

2. Release of plant-food elements from soil minerals by chemical reaction and formation of new soluble compounds containing the plant-food elements.

3. Corrective of excessive magnesium in the soil. Excess of magnesium over calcium in soil is stated to prevent proper development of plants, and calcium compounds are added to soils to bring about the proper ratio between these two elements.

4. Flocculant of clay soils. Calcium compounds coagulate the colloidal material of the clay, bringing about a granular condition of the soil and markedly improving the tilth.

5. Assistant of bacterial action. Beneficial bacteriological processes are said to be greatly helped by an abundant supply of calcium compounds in the soil.

6. Converter of toxic compounds of aluminum, which become soluble in strongly acid soils, into insoluble and harmless compounds.

Limestone and Dolomite

Limestone and dolomite are used for fertilizers, either directly in a finely ground condition, or, after calcination, as burned lime, air-slaked lime, or water-slaked lime.

Limestones range from high-calcium limestones with a maximum of 56 percent CaO through the magnesian limestones to dolomites containing theoretically 30 percent CaO, 22 percent MgO, and 48 percent CO_2. Even high-calcium limestones, however, usually contain some magnesium, and dolomites never contain quite 22 percent MgO. Limestones, moreover, are never pure carbonates but always contain impurities, chiefly silica, iron oxide, and alumina. Analyses of agricultural limestones vary greatly, ranging from 98 percent $CaCO_3$, a very pure limestone, to as low as 54 percent $CaCO_3$ with 44 percent $MgCO_3$, a dolomitic limestone.

Pulverized limestone for agricultural use is produced at many plants. Normally a large proportion of agricultural limestone is produced in the course of regular operations at commercial crushed-stone and building-stone

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plants, although in seasons of increased demand for agricultural limestone some producing plants have resorted to auxiliary pulverizers to increase their supply. Demand is said to be overtaking byproduct supply, and direct production is becoming more and more necessary. In localities where agricultural limestone is the only product of the quarry, the product is usually reduced in jaw or gyratory crushers to 2- to 2½-inch size and then ground to the proper size for agricultural use in hammer mills, although other types of grinding mills are also employed successfully. The limestone is dried before pulverizing at some plants.

Separate production figures for agricultural limestone are not available, but sales of pulverized limestone for agricultural use are reported for the years since 1911. Growth in sales of limestone for this use has been very rapid, rising from 174,290 short tons in 1911 to a maximum of 2,654,580 tons in 1929. Sales in recent years are given in the following table:

Agricultural pulverized limestone sold or used by producers[1/]

Year	Quantity (short tons)	Value	Average value per ton
1924	1,352,600	$2,046,860	$1.51
1925	1,954,480	2,880,589	1.47
1926	1,850,620	3,064,235	1.66
1927	2,206,470	3,360,704	1.52
1928	2,186,870	3,153,848	1.44
1929	2,654,580	3,764,775	1.42
1930	2,542,100	3,309,329	1.30
1931	1,421,050	2,117,141	1.49
1932	910,430	1,229,107	1.35
1933			

1/ Mineral Resources of the United States, part II (annual), U. S. Bureau of Mines; and Minerals Yearbook, U. S. Bureau of Mines (years 1932 and 1933).

Annual sales of agricultural limestone by States are also available. In recent years Illinois, Iowa, Ohio, Kentucky, Indiana, Michigan, Tennessee, Virginia, and Missouri have been the outstanding producers of limestone for this purpose.

The principal markets for agricultural limestone are in the North Central States from Missouri and Kansas north and east to Ohio. Illinois is the leading consuming State. The demand is highly seasonal. Normally August, September, and October are said to develop at least 75 percent of the demand, with a minor peak in March if the spring is open and favorable.

Specifications for agricultural limestone are not rigid. Usually the material should contain at least 95 percent of calcium and magnesium carbonates. There is a difference of opinion as to the value of magnesian limestone and

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dolomites for this purpose. Most of the ground limestone used on soils, however, does not contain more than 10 percent of magnesium carbonate. Screen sizes are quite variable. The ground limestone varies from a product passing a 4-mesh screen to one all of which passes through a 100-mesh screen. The standard size is said to be that which will pass a 10-mesh screen. The color of the marketed product ranges from white to gray.

Agricultural limestone is sold both in bulk and in bags. Various market channels have been employed. Direct mail selling, selling through agents on the road, through dealers, brokers, and local county farm bureaus, have all been used. In Illinois the largest single outlet has been through the local county farm bureaus.

The price of agricultural limestone at commercial crushing plants ranges from 25 cents to $2.50 a ton in carload lots, depending upon the character of the material marketed. As indicated in the foregoing table the average value per short ton of the agricultural limestone sold in the United States has ranged in recent years between $1.30 and $1.66.

Lime

Calcination of limestone drives off the carbon dioxide content, leaving a residue of calcium oxide, which is known as burned lime or quicklime. Treatment of this residue with water produces water-slaked lime or hydrate of lime. If the quicklime is left exposed to the air it absorbs moisture and carbon dioxide and is called air-slaked lime.

Both quicklime and hydrated lime are used as soil amendments and plant foods. Quicklime is the most concentrated form in which calcium can be applied to the soil, while the hydrate of lime is the most finely pulverized form of lime possible to obtain.

The percentage of calcium oxide present in fresh quicklime depends upon the purity of the original carbonate material used and upon the completeness of the calcination. When freshly prepared for agricultural use quicklime contains 60 to 90 percent of calcium oxide (CaO). If prepared from limestone containing magnesium the lime may contain 10 to 40 percent MgO (magnesium oxide), with correspondingly lower CaO content. Pure water-slaked lime contains a maximum of 75.7 percent CaO. Slaked lime prepared from magnesian limestone contains magnesium hydroxide, which is only slightly soluble in water. Air slaked lime may contain as much as 75 percent of calcium oxide, but it varies greatly and is practically all calcium carbonate and identical with finely ground limestone if it has been exposed long to the air.

Quicklime appears on the market either in lumps (just as it comes from the kiln) or pulverized to any desired fineness. It is chalk white to grayish brown. Lump lime is shipped in bulk, in wooden barrels of 180 to 280 pounds net capacity, or in iron casks holding 400 pounds. Ground lime is shipped in waterproof paper-burlap bags holding 90 or 180 pounds and in air-tight iron casks. Hydrate of lime is a very fine, dry, white powder; it is shipped in 50-pound paper sacks, in 100-pound burlap bags, and in paper-lined wooden barrels.

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Virtually all of the lime produced in the United States at present is burned in some form of kiln. Although both shaft and rotary kilns are in use, the shaft kiln is generally preferred. In 1927, out of 1,546 active kilns in the United States, 1,192 were shaft or vertical kilns. Lime burning is a continuous process, limestone being charged in lumps ranging from 4 inches in diameter to as large as one man can handle. Wood, coal, or gas may be used for fuel. Hydrated lime is prepared by crushing the lump lime from the kiln to 1-inch diameter or less and mixing it with water in a hydrator; the hydrated lime produced is screened and stored.

Sales of quicklime for agricultural use in recent years, as shown in the accompanying table, have exhibited a general declining tendency since 1925, both in quantity and value. On the other hand, sales of hydrated lime rose gradually in volume, although declining in average value. In 1932, 71 percent of the agricultural lime sold in the United States was hydrated lime and only 29 percent was quicklime. Pennsylvania was by far the largest producer of agricultural lime in 1932, with 127,586 short tons. Ohio (40,200 tons), Maryland (26,050 tons), Virginia (12,089 tons), and West Virginia (9,967 tons) were other large producing States.

The average value of quicklime in recent years has ranged from $4.78 to $6.10 and of hydrated lime from $5.92 to $9.04. The price trends are shown in the accompanying table.

Calcareous Marls

Calcareous marls are usually unconsolidated deposits consisting of varying proportions of sand or clay, with important amounts of calcium carbonate, which may form from 5 to 95 percent or more of the whole material. Fresh-water marls, which occur in the basins of existing or extinct lakes, are composed almost entirely of calcium carbonate and form white to dark gray, fine, granular, loose, noncoherent deposits. Calcareous marls of marine origin occur in the Atlantic and Gulf of Mexico coastal plains.

Calcareous marls are used as liming materials. Preparatory treatment is relatively simple; at the most, drying in rotary driers, where the moisture content is high or the material is plastic and lumpy, and then pulverizing.

Domestic sales of calcareous marls for agricultural use since 1916, when they were first stated separately, have ranged between 11,575 and 99,410 short tons. The maximum was reached in 1923; and subsequently there has been a generally downward trend, reaching 11,575 tons in 1932. The average value per ton of the annual sales in these 17 years has remained between $2.24 and $3.58.

Fresh-water marls have been produced in recent years in Arkansas, California, Illinois, Maine, Maryland, Michigan, Minnesota, Montana, Nevada, New York, North Carolina, Ohio, Pennsylvania, South Carolina, Utah, Virginia, West Virginia, and Wisconsin. Marine marls, composed of loose or partly consolidated fragments of marine shells, have been dug in the coastal plain of North Carolina and South Carolina.

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Sales of agricultural lime from limestone[1/]

Year	Quicklime				Hydrated lime				Total lime			
	Quantity, gross short tons	Effective lime content	Total value	Ave. value	Quantity, gross short tons	Effective lime content	Total value	Ave. value	Quantity, gross short tons	Effective lime content	Total value	Ave. value
1924	119,926	100,700	$703,692	$5.87	128,410	89,900	$1,160,822	$9.04	248,336	190,600	$1,864,514	$7.51
1925	132,011	110,800	744,518	5.64	166,965	116,900	1,384,651	8.29	298,976	227,700	2,129,169	7.12
1926	112,717	94,600	687,661	6.10	184,293	129,000	1,465,572	7.95	297,010	223,600	2,153,233	7.25
1927	107,866	90,530	615,789	5.71	215,027	150,500	1,622,082	7.54	322,893	241,030	2,237,871	6.93
1928	110,533	93,000	639,615	5.79	223,377	156,000	1,647,943	7.38	333,910	249,000	2,287,558	6.85
1929	89,654	75,400	448,634	5.00	248,675	165,000	1,939,267	7.80	338,329	240,400	2,387,901	7.06
1930	91,521	77,000	512,383	5.60	251,590	167,000	1,860,396	7.39	343,111	244,000	2,372,779	6.92
1931	78,392	66,000	422,107	5.38	218,920	145,000	1,502,042	6.86	297,312	211,000	1,924,149	6.47
1932	71,858	60,500	343,501	4.78	172,716	114,400	1,023,270	5.92	244,574	174,900	1,366,771	5.59
1933									231,000			

1/ Mineral Resources of the United States, Part II (annual), U. S. Bureau of Mines, and Minerals Yearbook, U. S. Bureau of Mines (for years 1932 and 1933).

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Sales of calcareous marl in the United States[1/]

Year	Marine marl			Fresh-water marl			Total		
	Quantity, short tons	Total value	Ave. value	Quantity, short tons	Total value	Ave. value	Quantity, short tons	Total value	Ave. value
1916	9,641	$ 18,423	$1.91	48,447	$126,345	$2.60	58,088	$144,768	$2.49
1917	25,986	53,148	2.05	47,914	112,075	2.34	73,900	165,223	2.24
1918	40,873	112,209	2.75	57,821	148,873	2.57	98,694	261,082	2.65
1919	(2)	(2)	(2)	(2)	(2)	(2)	91,437	327,294	3.58
1920	(2)	(2)	(2)	(2)	(2)	(2)	97,487	322,339	3.31
1921	(2)	(2)	(2)	(2)	(2)	(2)	59,730	195,743	3.28
1922	(2)	(2)	(2)	(2)	(2)	(2)	67,777	203,196	3.00
1923	---	---	---	99,410	328,932	3.31	99,410	328,932	3.31
1924	---	---	---	72,710	225,383	3.10	72,710	225,383	3.10
1925	---	---	---	68,670	187,839	2.74	68,670	187,839	2.74
1926	---	---	---	55,060	146,094	2.65	55,060	146,094	2.65
1927	---	---	---	52,692	180,166	3.40	52,692	180,166	3.40
1928	---	---	---	61,034	200,704	3.29	61,034	200,704	3.29
1929	---	---	---	38,990	130,866	3.36	38,990	130,866	3.36
1930	---	---	---	34,012	112,523	3.31	34,012	112,523	3.31
1931	---	---	---	25,056	65,935	2.63	25,056	65,935	2.63
1932	---	---	---	11,575	28,000	2.42	11,575	28,000	2.42

1/ Mineral Resources of the United States, Part 2, (annual), U. S. Geological Survey and Bureau of Mines, and Minerals Yearbook, U. S. Bureau of Mines (for year 1932).
2/ Data not available.

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Gypsum and Anhydrite

Agricultural gypsum, or land plaster, as it was formerly called, is obtained by grinding and pulverizing the natural rock or mineral known as gypsum ($CaSO_4.2H_2O$), 79.1 percent of which is calcium sulphate and the balance (20.9 percent) water of crystallization. The pure mineral consists of 32.5 percent lime (CaO), 46.6 percent sulphur trioxide, and 20.9 percent water.

Gypsum is a very common mineral; commercial deposits are widely distributed in the United States and occur in New York, Virginia, Ohio, Michigan, Iowa, South Dakota, Kansas, Oklahoma, Texas, Montana, Wyoming, Colorado, New Mexico, Utah, Arizona, Nevada, and California. In geologic age the deposits range from Silurian to Quaternary. The most extensive deposits in the United States, those in the Western States, occur in the Pennsylvania, Triassic, and Jurassic rocks. Gypsum occurs in various types of deposits - interbedded, efflorescent, periodic-lake, veins, and dunes. Bodies of gypsum interbedded with other sedimentary rocks are the type of greatest economic value. Efflorescent deposits (gypsite or earthy gypsum) are formed at the surface by the evaporation of percolating gypsum-bearing waters. Periodic lake deposits are formed by crystallization from shallow, intermittent lakes.

Agricultural gypsum is produced at numerous plants distributed over the United States. Sales of gypsum for agricultural purposes are shown in the accompanying table. In 1932, only about 1 percent of the gypsum mined in the United States was sold for use as agricultural gypsum. Sales by States are not available in recent years.

The treatment of the mined or quarried product before marketing is simple. The gypsum is crushed to a small size, where necessary, dried (but not calcined) and then pulverized to a whitish powder, 5 to 100 mesh or even finer screen size.

Prices for agricultural gypsum in recent years are shown intthe following table.

Sales of domestic agricultural gypsum in the United States[1/]

Year	Quantity, short tons	Total value	Average value per short ton
1924	22,298	$125,612	$5.63
1925	26,001	153,902	5.92
1926	27,294	151,916	5.57
1927	29,452	129,825	4.41
1928	25,668	90,937	3.54
1929	38,099	161,288	4.23
1930	31,029	158,538	5.11
1931	28,350	138,725	4.89
1932	15,664	89,086	5.69
1933	11,479	63,892	5.57

1/ Mineral Resources of the United States, Part 2, (annual), U. S. Geological Survey and Bureau of Mines, and Minerals Yearbook, U. S. Bureau of Mines (for years 1932 and 1933).

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Prices of agricultural gypsum, per short ton, in carload lots, f.o.b. mill

	Rock Products						Eng. and Mining Journal
Year	Los Angeles, Calif.	San Francisco, Calif.	Seattle, Wash.	Centerville, Iowa	Grand Rapids, Mich.	Gypsum, Ohio	U. S. (depending upon location)
1926	$8.00-10.40	$12.00-14.00	$10.00-11.00	$15.00	$6.00	$6.00	$6-12
1927	8.00	9.00-11.65	10.00-11.00	15.00	6.00	6.00	6-15
1928	8.00	9.00	10.00-10.50	15.00	6.00	6.00	4-15
1929	6.00- 9.50	9.00	9.00-10.50	6.00-15.00	4.00-7.00	6.00	4-9
1930	7.00- 9.00	---	9.00	6.00	7.00	---	4-8
1931	---	---	---	---	---	---	6-7
1932	---	---	---	---	---	---	6-7
1933	---	---	---	---	---	---	6-7

Domestic production of crude gypsum is supplemented by imports. In recent years over 90 percent of these imports have come from Canada and most of the balance from Mexico. The crude gypsum imported from Canada is destined mainly for manufacture at plants along the Atlantic coast, although approximately 10 percent is said to be sold or used as a retarder in the manufacture of portland cement and 9 percent (mainly in the form of anhydrite) as agricultural gypsum. The Mexican gypsum goes to Pacific coast ports. Imported crude gypsum sold or used for agricultural purposes, as reported by the importers in recent years, is shown in the accompanying table. The figures for 1932 are more complete than in the immediately preceding years, the statistics for that year covering several fertilizer importing plants for which figures had not previously been included.

The total annual consumption of gypsum for agricultural purposes in the United States is roughly indicated by the sum of the domestic sales for agricultural purposes and the sales of imported crude gypsum for a similar purpose. In 1932 the total thus obtained was 47,424 short tons. About a third of the crude gypsum employed as fertilizer in the United States is used in eastern Virginia and North Carolina in growing the Virginia, or Jumbo, peanut. Smaller quantities are used in Georgia, Alabama, and Texas in growing the smaller Spanish peanut. For most crops, but particularly for alfalfa, considerable quantities of agricultural gypsum are used in Washington and Oregon, where the soil in many localities is deficient in sulphate sulphur, and this deficiency is met by the use of finely ground gypsum. In California and some other Western States considerable quantities of gypsum are used to neutralize black alkali.

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Imports

Sales in the United States of foreign gypsum for agricultural purposes, as reported by the importers

Year	Quantity, short tons	Value	Average value per short ton
1924	18,200	(1)	(1)
1925	(1)	(1)	(1)
1926	(1)	(1)	(1)
1927	32,278	$191,575	$5.94
1928	2/ 34,678	2/ 181,206	2/ 5.23
1929	2/ 28,263	2/ 163,754	2/ 5.79
1930	2/ 27,443	2/ 154,857	2/ 5.64
1931	17,353	93,648	5.40
1932	31,760	166,944	5.26
1933	40,847	186,072	4.56

1/ Data not available.
2/ Includes sales "for other uses." These ranged in other recent years from 1,790 to 12,579 short tons.

Gypsum serves both as a direct and an indirect fertilizer. In the first capacity it supplies two of the essential plant foods - calcium and sulphur. In the latter it is said to act as a preserver of nitrogen in barnyard manure (by fixing the volatile ammonia); to increase the activity of the nitrogen-fixing bacteria of the soil; to set free other plant foods in the soil through reaction with insoluble mineral matter containing these elements; to act as a specific for black alkali, transforming the harmful sodium carbonate of the black alkali soils into the less harmful sodium sulphate; and to loosen clay soils through flocculation of the fine material.

These are substitutes for some of the uses of the natural gypsum. Anhydrite ($CaSO_4$), a mineral closely allied to gypsum in character and origin, though lacking water of crystallization, may be used as a fertilizer in place of gypsum, its lower solubility being overcome by finer grinding. Already several thousand tons are being imported into the South Atlantic States from Canada annually for fertilizing peanuts, and it is also a constituent of some commercial fertilizers. Anhydrite deposits are found at many places in the United States in close association with gypsum deposits. Artificially prepared gypsum is available chiefly from two sources - the superphosphate industry and the synthetic gypsum industry - although some other industries also yield it. Superphosphate is a mixture of monocalcium phosphate and hydrated calcium sulphate (gypsum). Most superphosphates contain about half their weight as gypsum. Much more gypsum might be used as a fertilizer were it not for the use of the gypsum containing superphosphate, the amount of gypsum present being sufficient for some soils and some crops. Synthetic gypsum is produced at several domestic plants. Various substitute sources exist for the calcium and sulphur contents of gypsum.

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COPPER

Copper is applied to the soil only as a direct fertilizer, as a plant nutrient, solely to supply essential copper to plants where it is either not present in the soil or at least not available. Copper sulphate is the only copper compound used.

Copper occurs normally in most productive soils, although present in relatively minute amounts. It has been found to be deficient, however, in certain peat soils, particularly those of the Florida Everglades, and in certain sections of New York and Michigan. There is evidence of copper deficiency also in other soils, as in the Florida citrus regions. These deficiencies, whether indicated by the failure of crops to grow, as on the peat soils, or by the presence of characteristic physiologic diseases, as the die-back of citrus trees, are corrected by the application of small quantities of copper compounds. Where excessive amounts have been used, injury to the plants has been reported.

Copper Sulphate

Copper sulphate, or blue vitriol, is used as a plant nutrient and is the principal source of copper for agricultural purposes.

In stimulating crop production in the Florida Everglades it has been applied both in connection with fertilizer mixtures and separately, in quantities ranging from 30 to 50 pounds per acre per year for most crops, although up to 100 pounds per acre has been reported used on the sugar-cane lands of this region. Excessive amounts of copper sulphate are reported to be injurious to crops.

In the treatment of "die-back" (exanthema) in the Florida citrus trees crystals of copper sulphate were originally placed under the bark of the tree, but in recent years the copper sulphate has been applied in fertilizers or separately to the soil, in amounts ranging from 50 to 75 pounds per acre per year, or in some cases spread on the soil under the trees in amounts of 1/4 pound to 1 pound to the tree, depending on the size of the tree. It has also been sprayed on the trees as a constituent of Bordeaux mixture. In California small quantities of powdered copper sulphate placed in holes bored in the base of tree trunks are said to have successfully controlled exanthema.

Copper sulphate is obtainable in the technical or ordinary commercial grade and also in C. P. and U. S. P. grades. It is packed in 1- and 5-pound bottles, 25- and 50-pound boxes, 100-pound kegs, and 250; 350; 450, and 500-pound barrels. Wholesale prices in barrels at works ranged from $3.00 to $3.75 per 100 pounds in 1933 and rose from $3.75 to $3.85 early in 1934, according to Chemical Industries. In June 1934 quotations in the Oil, Paint & Drug Reporter for copper sulphate, 99 percent, crystals, f.o.b. New York, in barrels, ranged from $4.55 per 100 pounds for 1 or 2 barrels to $4.00 per 100 pounds for lots of 16 to 25 barrels.

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IRON

Iron is definitely recognized as essential for the growth of plants; its absence causes a pathological chlorosis, as it is needed in the formation of chlorophyll in the green parts of the plants. The amounts required, however, are exceedingly small, and enough iron is present in practically all soils to meet ordinary needs. Iron salts, therefore, do not have to be used as plant foods, except in unusual circumstances, where iron either is deficient in the soils or is not available to the plants, due to an excess of manganese or calcium.

The sandy soils of northern Michigan are said to be deficient in iron. Certain acid pineapple soils in Hawaii which have a very high iron content

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have also an abnormally high manganese content which renders the iron content unavailable to the pineapple plants. On certain alkaline limestone soils, as in Puerto Rico, a lime-induced chlorosis occurs, resulting from the unavailability of the iron in the soil. Applications of iron salts to the plants in these cases correct the chlorosis and restore the health and normal vigor of the plants.

Ferrous Sulphate

The only iron compound used at present as a plant food is ferrous sulphate or copperas. It is used commercially in the successful treatment of the manganese-induced iron-deficiency chlorosis of pineapples in Hawaii. The most economical and effective treatment is stated to be 3 or 4 applications of a 6-percent solution of the iron sulphate (25 pounds of copperas to 50 gallons of water) sprayed from above on the plants, at the rate of about 10 pounds of copperas per acre per spraying. The iron is said to be applied frequently to the plant during periods of rapid growth, but comparatively few sprayings are made during quiescent periods. Plants are sprayed whenever there is any indication of yellowing or of failing vigor. The cost of spraying is considered negligible in comparison with the other expenditures necessary in the raising of pineapples. With an experimental sprayer the cost amounted to approximately 60 cents an acre per spraying. All the Hawaiian pineapple planters have adopted this treatment, and many thousands of acres of manganiferous soils are thus treated; it is reported to be used regularly on over half of the Hawaiian pineapple fields.

In Hawaii the addition of solutions of iron salts or of solid iron salts to the soil itself appeared of little value. In Puerto Rico, however, on lime-induced chlorosis of pineapple plants the application of crystals of ferrous sulphate to the roots was effective, but the spraying of ferrous sulphate solution on the soil was of no use. Treatment of the leaves of the pineapple plants in Puerto Rico with iron salts (ferric chloride and ferrous sulphate) was effective, but the commercial success of the ferrous sulphate treatment under Puerto Rican conditions was considered doubtful.

Ferrous sulphate is marketed in 1- and 5-pound bottles, 1- and 5-pound cans, 25-pound boxes, 100-pound kegs, 200-pound bags, 400- to 425-pound barrels, and carload lots. Grades obtainable are technical, C. P., U. S. P., and sugar sulphate (anhydrous).

Ferrous sulphate (copperas), crystals and granular, car lots, at works, was quoted in June 1934, according to the Oil, Paint & Drug Reporter, in bulk at $12 to $13 per ton; in bags at $14 to $15 per ton; and in barrels at $16 to $17 per ton. U. S. P. crystals of iron sulphate were prices at $0.03¾ to $0.04 per pound.

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MAGNESIUM

Magnesium is present in varying amounts in all agricultural soils, ranging from traces to high percentages, generally in much smaller quantities than calcium. Relatively few soils are deficient in magnesium, but to such soils magnesium has been added as magnesium sulphate (epsom salts), potassium-magnesium sulphate, and magnesium carbonate with beneficial results. Magnesium deficiency occurs especially in the lighter sandier soils of the Atlantic seaboard and the southeastern and Gulf coastal plains and is also known in Maine, Connecticut, and other States. Magnesium is now being used extensively as a plant food on tobacco and potatoes and has given good results on cotton, corn, and other crops.

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Most liming materials used in agriculture contain magnesium in varying amounts, so that magnesium is often unintentionally added to the soil in sufficient amounts to correct any minor deficiency.

Three compounds of magnesium are available at reasonable cost - sulphate of potassium-magnesium, commercial magnesium sulphate, and dolomite, or magnesian limestone. Soluble magnesium carriers, such as magnesium sulphate and potassium-magnesium sulphate, are reported to be more effective than relatively insoluble compounds, such as dolomite and magnesite.

Magnesium compounds serve also as indirect fertilizers. The magnesium compounds in limestone, magnesium limestone, and dolomite and their calcined products are said to act much like the corresponding calcium compounds in neutralizing soils and producing other effects resulting from the use of calcium compounds. Magnesium compounds, however, commonly are not deliberately added as indirect fertilizers because of their magnesium content. However, an interesting example of the use of magnesium sulphate for reclaiming a greenhouse soil has been describe in England.6/ Water containing sodium chloride had converted part of the soil to sodium clay, rendering it unproductive, but by adding 10 cwt. of magnesium sulphate per acre a base exchange took place, and the sodium sulphate could be leached out.

Two grades of epsom salts are commonly produced and marketed, the U. S. P. grade (practically chemically pure) and the technical grade, which is at least 90 percent pure. The salts are usually shipped in wooden barrels but sometimes in 100-pound burlap bags.

Epsom salts are sold wholesale at a price per 100 pounds, f.o.b. the principal markets. In June 1934 in the New York market the wholesale price of domestic epsom salts, U. S. P. grade, was $2.15 per 100 pounds, in bags, in carload lots, and $2.25 in barrels, and the technical grade was listed at $2.10 per 100 pounds in bags and $2.20 per 100 pounds in barrels, according to the Oil, Paint & Drug Reporter.

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MANGANESE

Manganese is generally considered an essential element in plant growth. The amount needed is quite small, and where manganese is available to the plant in excessive amounts, toxicity results. In most American soils manganese is present and available in sufficient quantity for crop production, but its scarcity in some soils, such as the unique alkaline calcareous soils of the Everglades in Dade County, Fla., and its unavailability in overlimed areas of naturally manganese-bearing soils, as in parts of the Atlantic coastal plain of North Carolina, make it a limiting element in plant growth. Manganese applications are required as the first essential to successful crop production in these instances.

Manganese is used only as a direct fertilizer, a plant nutrient, and only where there is a deficiency of available manganese for the plant. Many manganese carriers have been tried in fertilizer experiments, but the naturally occurring manganese ores or manganese-bearing materials tested have

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failed generally to correct the effects of manganese deficiency in plants. The iodide, nitrate, chloride, and sulphate of manganese have also been tried. The sulphate has given the best results and is the only salt of manganese now in commercial use as a fertilizer. Barnyard manure contains appreciable amounts of manganese, and the increasing scarcity of manure in the United States is undoubtedly a factor in the increase in manganese deficiency noted in recent years.

Manganese Sulphate

The sulphate is used as a source of manganese for plant nutrition on neutral and alkaline soils deficient in available manganese. It is used most extensively in the Everglades region of southern Florida, stimulating the growth and combatting chlorosis of such crops as beets, carrots, tomatoes, cabbage, lettuce, corn, potatoes, beans, ornamentals, and forage crops, which formerly were considered failures on the calcareous and muck soils of that area. Its use in southern Florida about 1927 appears to have been the first commercial use of manganese sulphate as a fertilizer, although it had been used experimentally for a number of years before. Manganese sulphate has been applied alone to the soil, sprayed on the plant, mixed with commercial fertilizers, or mixed with compost. Ordinarily it is mixed with commercial fertilizer. From 50 to 100 pounds of manganese sulphate are ordinarily used per acre.

Manganese sulphate is produced commercially by evaporation and crystallization of aqueous manganese sulphate solutions, the salt crystallizing with 1 to 7 molecules of water. The monohydrate, $MnSO_4.H_2O$, crystallizes from hot solutions (27° to 100°C.); the tetrahydrate, $MnSO_4.4H_2O$, from solutions of 20° to 30°C.; the pentahydrate, $MnSO_4.5H_2O$, from solutions of ordinary temperatures, 7° to 20°C; and the heptahydrate, $MnSO_4.7H_2O$, from low-temperature solutions, -4° to 6°C. The monohydrate is pale reddish yellow; the others are pale red. Their manganese content ranges from 19.8 to 32.5 percent in the different forms. In the tetrahydrate it is 23.6 percent. Heated to redness these hydrated manganese sulphates change to the white, friable, anhydrous salt ($MnSO_4$).

The raw materials for the preparation of the manganese sulphate solutions are the oxide and carbonate ores of manganese. The carbonate is dissolved directly in sulphuric acid with the formation of the manganese sulphate solution. The black oxide, MnO_2, is heated with coal to reduce it to the monoxide, which is then dissolved in sulphuric acid with the formation of manganous sulphate; or it is heated with ferrous sulphate or strong sulphuric acid and converted to manganous sulphate, which is leached out with water. It is also recovered as a byproduct in chemical processes involving the use of manganese ores.

The hydrated manganese sulphate of commerce consists of pale rose-red, translucent, efflorescent crystals or a pink to whitish powder, very soluble in water. It is marketed in technical and C. P. grades and is obtainable in 1- and 5-pound bottles, 25-pound boxes, 100-pound bags, 375-pound barrels, and 600-pound casks. Commercial manganese sulphate suitable for use as a fertilizer

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has been available in recent years at prices ranging from 5 to 10 cents a pound. In June 1934 manganese sulphate was quoted in the Oil, Paint & Drug Reporter, at works, in barrels, at 5 to 5½ cents a pound. Anhydrous manganese sulphate, at works, in barrels, was listed at 9 to 9½ cents a pound.

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SULPHUR

Sulphur and its compounds are used both as direct and indirect fertilizers, but the major fertilizer use of this element is as a plant nutrient. Where sufficient quantities of available sulphur are not present in the soil it is considered the limiting factor in plant growth.

Most soils are not deficient in this essential plant nutrient, although the average sulphur content is relatively small and is continually being reduced by drainage and cropping. Rainfall supplements the soil sulphur supply, and large quantities of sulphur are incidentally furnished by the more commonly used fertilizer materials, such as superphosphate, ammonium sulphate, and potassium sulphate, which appear in most regions to supply all the needed sulphur. However, notable deficiencies of sulphur are now known to exist over rather extensive areas in Oregon, Idaho, and Washington. Other soils responding to sulphur-carrier treatment have been found elsewhere in the United States and in other parts of the world.

As indirect fertilizers, sulphur and its compounds are said to have various functions, including the correction of black alkali soils, reaction with soil constituents and release of the nutrient elements, soil ameliorant resulting from the flocculating effect, and the control of the reaction of the soil.

The element is applied to the soil as a fertilizer in the form of native sulphur and sundry combined forms. Inorganic combinations are usually sulphates, such as gypsum, anhydrite, superphosphate (which contains synthetic

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gypsum), ammonium sulphate, and potassium sulphate. Organic combinations are complex compounds derived from plant and animal sources.

Native Sulphur

Although sulphur had been known to be an essential element for plant growth for many years, it was not until 1912 that elemental sulphur was shown to be of value as a plant food as a result of the work of several foreign experimenters. Subsequently fertilizer experiments with elemental sulphur were conducted in Oregon, Texas, Florida, and other parts of the United States. Commercial use of elemental sulphur as a fertilizer followed in the western portions of the United States, as in the semi-arid portions of Oregon. The total annual consumption of elemental sulphur, however, is relatively small. In the central and eastern portions of the United States it has not been used, as the fertilizers already in use are believed to contain sufficient available sulphur.

Of the various commercial grades of sulphur on the market, only those finely divided varieties, flowers of sulphur and commercial flour sulphur, are said to be used for direct application to the soil as a plant food. Flowers of sulphur is crude sulphur refined by sublimation and caught in dust form. Commercial flour sulphur is crude sulphur ground and sized. Its fineness ranges from 50 to 99 percent through 200-mesh up to 99 percent through 300-mesh, depending on the brand. Activating agents are sometimes added to hasten the oxidation of the sulphur and produce earlier results. The elemental sulphur is applied alone or inoculated with sulphur-oxidizing bacteria, or else added to composts as a fertilizer.

The fertilizing action of elemental sulphur is said to be due partly to favorable action on soil micro-organisms and partly to the formation, by oxidation by biological and chemical action, of sulphuric acid, which acts either directly as a source of sulphate sulphur for the plants or by its action on bases in the soil makes more mineral matter available to the plants.

The amounts of elemental sulphur applied to soils for crop production are stated to range from 40 pounds per acre per year up. On soils in southern Oregon, which contain only limited amounts of sulphur, and with crops requiring considerable sulphur for maximum production, 40 to 50 pounds per acre annually have given large increased yields. The application of elemental sulphur, even in small quantities, is said to increase the acidity of the soil and when large amounts are present to result in injury to plant life. It is also reported that elemental sulphur may be toxic through its incomplete oxidation by reason of the formation of intermediate toxic compounds.

As a soil amendment, elemental sulphur has diverse functions based upon the production of sulphuric acid through its oxidation. These functions include the control of soil acidity, the freeing of various elements by the action of the sulphuric acid upon soil compounds, the reclamation of black alkali land by the conversion of the harmful black alkali (sodium carbonate) into the much less harmful sodium sulphate ("white alkali") by the sulphuric

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acid, and the loosening and flocculating effect of the oxidized sulphur on heavy soils, and where flocculation and increased rate of percolation are necessary to wash out harmful accumulations of alkali.

Flotation sulphur as well as commercial flour sulphur and flowers of sulphur are said to be used as indirect fertilizers. In flotation sulphur 95 percent of the sulphur particles are said to be not over 3 microns (0.003 mm) in diameter, with a considerable portion approaching colloidal dimensions.

The Texas and Louisiana sulphur deposits supply nearly all the domestic consumption of native sulphur. By far the largest amount of domestic sulphur is sold as crude lump. Shipments are made in any quantity, but it is usually shipped in bulk in box cars or as whole ship cargoes. The amount shipped in sacks is almost negligible. Commercial flour sulphur (American), which is finely ground, crude run-of-mine sulphur, is usually shipped in 100-pound burlap sacks, either of single or double sacking. Where a sulphur dust is required, as for fertilizer purposes, this is the sulphur product usually used. Flowers of sulphur, sublimed refined sulphur in dust form, is usually marketed in 100-pound bags.

Sulphur is sold by the long ton, f.o.b. cars, mine, or ex vessel Atlantic seaboard. Export sulphur is largely sold f.o.b. Gulf ports. The primary marketing points are the mines. The sulphur is sold directly to the consumer, and shipments are made directly to him from the mines. Secondary marketing points are the Gulf ports, from which shipments are made to foreign countries, and the domestic Atlantic coast ports, whence shipments are again made by rail.

Prices of sulphur were, in June 1934, according to the Oil, Paint, & Drug Reporter, for crude, at mines, on contract, bulk, 1,000 long tons, $18 a ton, and for less than 1,000 tons, $20.00 a ton. Spot prices, near by, carlots, were $21.00 a ton; commercial flour sulphur, in bags, was quoted at $1.60 to $2.35 per 100 pounds, and in barrels at $1.95 to $2.70. Prices on flowers of sulphur were $3.00 to $3.75 per 100-pound bag and $3.35 to $4.10 per 100 pounds in barrels.

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(See also Gypsum (Calcium sulphate) references under Calcium.)

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ZINC

Zinc is used as a direct fertilizer, principally in the form of the sulphate, although metallic zinc, zinc oxide, and zinc chloride are reported also to have been used experimentally to correct nutritional disturbances due to apparent lack of zinc. The small quantity of zinc needed for maximum growth is available in most soils, but in the soils of certain areas, as the Everglades of Florida, the pecan regions of Georgia, Texas, and the Southwest, and the fruit-growing sections of California, deficiencies have been shown to exist by the presence of certain characteristic zinc-deficiency diseases, such as the pecan rosette, the mottle leaf of the citrus, and the little-leaf of deciduous fruit trees, all of which have been partly or wholly corrected by the addition of zinc salts.

Zinc Sulphate

Zinc sulphate may be used as a plant nutrient in four ways: (1) Sprayed on trees in solution; (2) applied directly to the soil; (3) injected into the trees in solution; and (4) placed as crystals in holes bored in tree trunks. Spraying seems to be the preferred and most successful method for treatment of diseased trees, with soil treatments next. In the case of pecans, the strongest sprays that have been used without injury to the foliage contained 2 pounds of zinc sulphate to each 100 gallons of water. With citrus fruits, sprays containing as little as 5 pounds of zinc sulphate to 100 gallons of water have caused damage, but zinc-lime sprays containing 10 pounds of zinc sulphate, 5 pounds of hydrated lime, and 100 gallons of water are reported to have caused no harm to the leaves.

In the soil treatment of pecans the best results have been reported with $\frac{1}{2}$ to $1\frac{1}{2}$ pounds of zinc sulphate for each inch of trunk circumference spread under the tree. With citrus trees the early practice of placing 5 to 10 pounds of zinc sulphate in a narrow band around the base of the tree has been reported as liable to cause injury to the tree, and the use of a few more pounds spread all over the ground under the drip of the tree suggested as safer.

In crop production in southern Florida, up to 12 pounds of zinc sulphate per acre is used. Experimental treatment of plants on the raw peat soils of the Everglades, using 49.5 pounds of zinc sulphate per acre, gave transient responses only, and evidences of zinc toxicity appeared in some instances.

The production of zinc sulphate in the United States amounts to only a few thousand tons a year, and probably only a very small fraction of this quantity is used for agricultural purposes. In 1931, marketed production was 5,290 short tons and in 1932, 4,252 short tons. Imports are a few hundred tons annually. Export figures are not available.

Crystallized zinc sulphate is marketed in the United States in 200-pound kegs and in 350-pound wooden barrels. It is also available in thin flake form. An anhydrous zinc sulphate is also marketed which is reported not to be anhydrous but to contain less water than the crystalline product.

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Wholesale price quotations on crystalline zinc sulphate, at New York, in bags or barrels, as reported by the Oil, Paint and Drug Reporter, have in recent years ranged between 2-5/8 and 3-1/2 cents per pound. It is the cheapest of the commercial zinc salts. In June 1934 it was listed at $2.65 to $2.80 per 100 pounds, in car lots.

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